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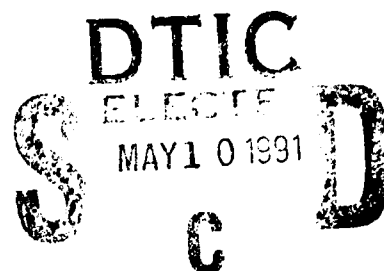
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**CATALYSTS AND INITIATORS AS INSTRUMENTS CONTROLLING  
STRUCTURE OF POLYMERS WITH INORGANIC BACKBONE**

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**K. Matyjaszewski**

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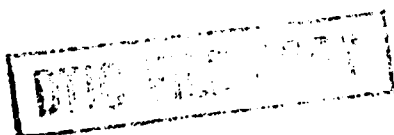
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<p>Importance of catalysts and initiators as factors which control macromolecular structure of various polymers with inorganic backbone is discussed. Chemoselectivity, regioselectivity, stereoselectivity and supramolecular control in the synthesis of polysiloxanes, polysilanes and polyphosphazenes is described.</p>					
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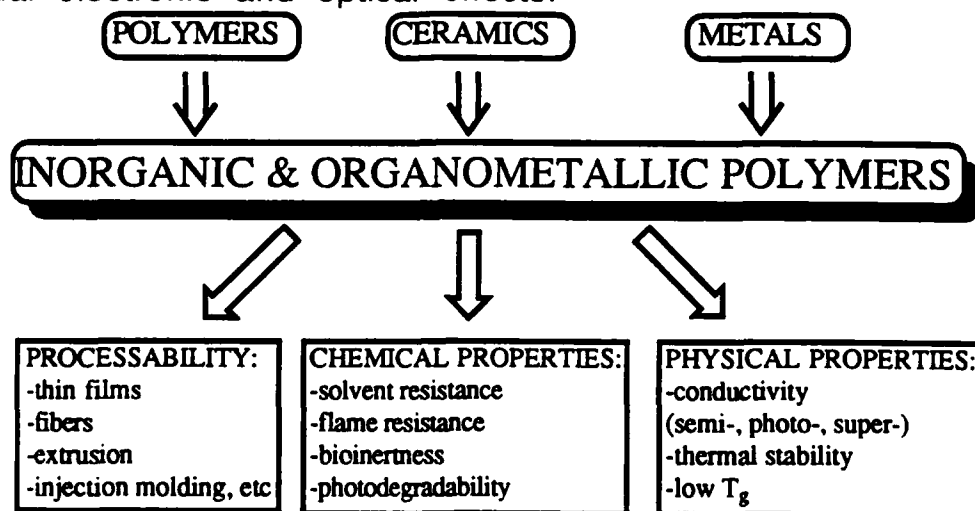
# CATALYSTS AND INITIATORS AS INSTRUMENTS CONTROLLING STRUCTURE OF POLYMERS WITH INORGANIC BACKBONE

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Three general methods for the synthesis of inorganic polymers: condensation, ring opening polymerization, and modifications are described. New catalyzed polymerization of phosphoranimines provides quantitatively low polydispersity, high molecular weight, linear polyphosphazenes at temperature below 100 °C. Polysilanes with low polydispersities are prepared by sonochemical reductive coupling. Ring-opening polymerization of strained cyclotetrasilanes provides first possibility of the tacticity control in polysilanes. Modification of polysilanes with triflic acid and various nucleophiles allows incorporation of functional groups to polysilanes and also synthesis of graft copolymers.

## INTRODUCTION

Inorganic and organometallic polymers belong to a new class of advanced materials located at the interphase of organic polymers, ceramics and metals<sup>1</sup>. Their unique chemical and physical properties and processability stimulate new applications. Some inorganic polymers behave as low temperature elastomers, some are fire and solvent resistant, some are bioinert, some have special surface properties, others show unusual electronic and optical effects:



However, at present, most inorganic and organometallic polymers are available as ill-defined materials with extremely high polydispersities (often with polymodal molecular weight

distribution), non-controlled degrees of polymerization and unknown structure of end groups. Some applications, particularly those in biomedical and optoelectronic fields, require well-defined polymers. Regular polymers are also necessary for structure-property correlations and as special model compounds. Some phenomena, such as formation of one dimensional superlattices<sup>2</sup> based on conducting polymers, can be observed only for very regular systems. Also, a microphase separation occurs in block and graft copolymers with controlled dimensions of segments. In this article possibilities of the improvement of the structural control of the inorganic and organometallic polymers will be discussed. Therefore, the correct choice of catalysts and initiators, which can improve control of macromolecular structure, is very important.

Most polymers with inorganic backbones are based on silicon: polysiloxanes, polysilanes, polysilazanes, and polycarbosilanes can serve as examples. Polyphosphazenes form another, commercially important, class of inorganic polymers. These linear inorganic polymers are true macromolecules with molecular weights above  $M_n > 100,000$  and sometimes even above  $M_n > 1,000,000$ . Usually they are soluble in common organic solvents and can be processed in a way typical for organic polymers (depending on structure of substituents). High molecular weight catenates of other elements such as germanium and sulfur are also known. Dialkyl substituted polygermanes resemble polysilanes. Polysulfur is thermodynamically stable only above its floor temperature ( $T > 160^\circ\text{C}$ ). In most other cases, cyclics dominate over linear chains. This is true not only for pure catenates (e.g. polyphosphines) but also for polymers with alternating structure of elements BN, BP, SiS, SiP, etc. Linear polymers are known for silazanes with small substituents (sometimes as small as hydrogen), cyclics are preferred even for permethylated systems. Polymerization of potentially strained four membered rings is not possible (silathianes) because larger elements can absorb angular deformations much easier than carbon. In some systems a polymer can be formed as a kinetic product which can be degraded to strainless cyclics under appropriate conditions, but, which can be sometimes sufficiently stable for some useful applications.

There are three general methods leading to inorganic polymers. They resemble classic methods known for organic polymers: condensation (usually step growth), ring opening polymerization (chain growth), and modifications. Double bonds

between two elements larger than carbon are not common (a few compounds with double bonds and with bulky substituents, e.g.  $R_2Si=SiR_2$ , are known<sup>3</sup> only for non-polymerizable systems) and, therefore, olefin-type polymerization is not applicable to inorganic polymers.

Some condensation reactions occur as pure step growth process (hydrolytic condensation of disubstituted dichlorosilanes to form polysiloxanes). However, in some other cases, reactivity of the end groups in growing polymer chains are very different from reactivities of a monomer and chain growth model operates (reductive coupling of dichlorosilanes with sodium to form polysilanes). In that case electron delocalization in the main chain facilitates reduction of long oligomers and polymers, which have higher electron affinity than a monomer. The main obstacle for the condensation process is formation of strainless cyclic oligomers.

Under special conditions strained rings can be formed and subsequently opened in the chain growth process. Here again, back-biting and formation of strainless cycles is the main challenge in the formation of well defined polymers. Correct choice of initiators and catalysts can lead, however, to polymers with regular structures. Anionic polymerization of hexamethylcyclotrisiloxane is probably the best example of living inorganic polymerization. Ring-opening polymerization of hexamethylcyclodisilazane yielded first known linear permethylated polysilazane<sup>4</sup>. Ring-opening of hexachlorocyclotriphosphazene is a commercially important process leading to polymers with molecular weights  $M_n \approx 1,000,000$ .

Modification of inorganic polymers is often used to exchange substituents, introduce special functional groups such as hydrophilic, lipophobic, electron rich/poor, mesogenic, bioactive, etc. Most modifications have been performed on polyphosphazenes (nucleophilic displacement of chlorines) and on partially hydrogenated siloxanes (hydrosilylation). Modifications of polysilanes is also known.

In this article the main emphasis will be put on the synthesis of polyphosphazenes and polysilanes with improved structural control and regularity.

### POLYSILOXANES

Polysiloxanes are the first type of polymers with an inorganic backbone in which high degree of structural control has

been achieved. The synthetic method best suited for the preparation of well-defined polysiloxanes is the anionic polymerization of hexamethylcyclotrisiloxane ( $D_3$ ) with a lithium counterion<sup>5</sup>. High molecular weight polymers ( $M_n \approx 100,000$ ) with low polydispersity ( $M_w/M_n < 1.1$ ) can be prepared in this way. Use of less strained monomer (octamethylcyclotetrasiloxane) and more bulky counterions ( $Na^+$ ,  $K^+$ ) is less chemoselective and a linear polymer is accompanied by various cyclics. Cationic polymerization is also accompanied by the formation of macrocyclics, mostly due to the end-biting reaction of the electrophilic active site with the silanol terminal groups<sup>6,7</sup>.

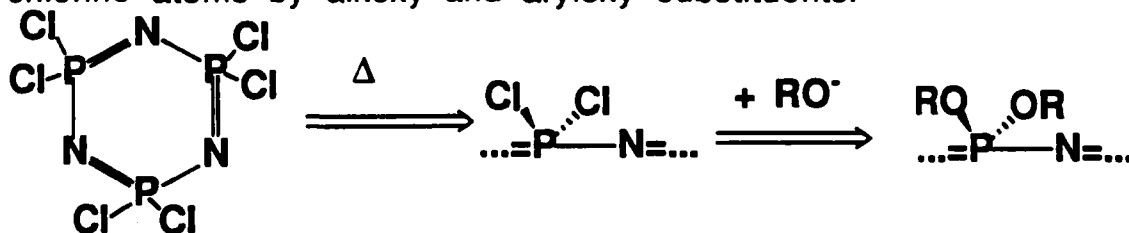
Poly(dimethylsiloxane) is probably the only siloxane polymer which does not form a mesophase and has only one first order thermal transition. Longer and larger organic substituents (diethyl, dipropyl, diphenyl) provide various crystalline phases and, in addition, a columnar mesophase typical for polymers with inorganic backbone<sup>8,9</sup>. The range of the mesophase increases strongly with the size of the organic substituent.

The living nature of  $D_3$  anionic polymerization allows formation of various block copolymers which phase separate very easily and produce materials with new morphologies<sup>10</sup>.

### POLYPHOSPHAZENES

Polyphosphazenes are interesting inorganic polymers which find applications as advanced materials with flexibility at a very low temperature, superb solvent and oil resistance, flame resistance, toughness, and vibration damping properties and also as potential biomaterials.<sup>11,12</sup> Polyphosphazenes are used as seals, gaskets, o-rings, fuel hoses, and as vibration shock mounts, serviceable over a wide range of temperatures and in harsh environments.

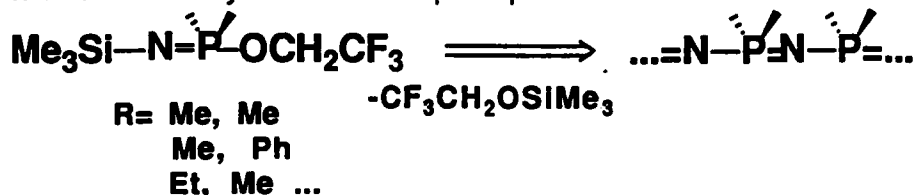
There are two main synthetic routes towards polyphosphazenes. The first is based on the ring-opening polymerization of hexachlorocyclotriphosphazene at approximately 250 °C and the subsequent displacement of chlorine atoms by alkoxy and aryloxy substituents.<sup>13</sup>



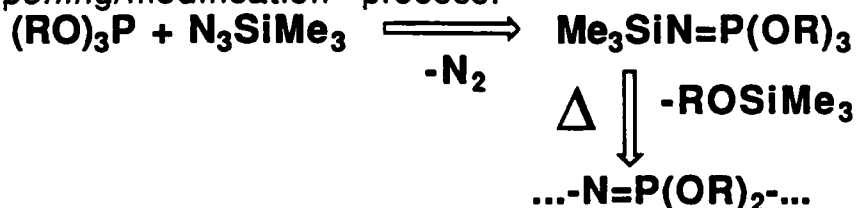
At present, this is the only process utilized commercially.

Unfortunately, this method leads to polymers with high polydispersities.<sup>14</sup> Application of Lewis and protonic acids as catalysts reduces polydispersities but also reduces molecular weights.<sup>15</sup> It is possible that milder reaction conditions reduce branching and crosslinking.

The alternative preparation of polyphosphazenes employs the high temperature (200 °C) condensation of N-silylphosphoranimines and provides polymers with alkyl and aryl substituents directly bound to phosphorus.<sup>16</sup>



Monomer synthesis is quite cumbersome and requires four steps with limited yields. The synthesis of phosphoranimines can be considerably improved in the case of trialkoxyderivatives which can be formed in one step from phosphites and trimethylsilyl azide.<sup>17, 18</sup> This Staudinger-type reaction provides in high yields phosphoranimines which can be thermally (200 °C) polymerized to polyphosphazenes, identical as formed in the classic Allcock's ring-opening/modification process:

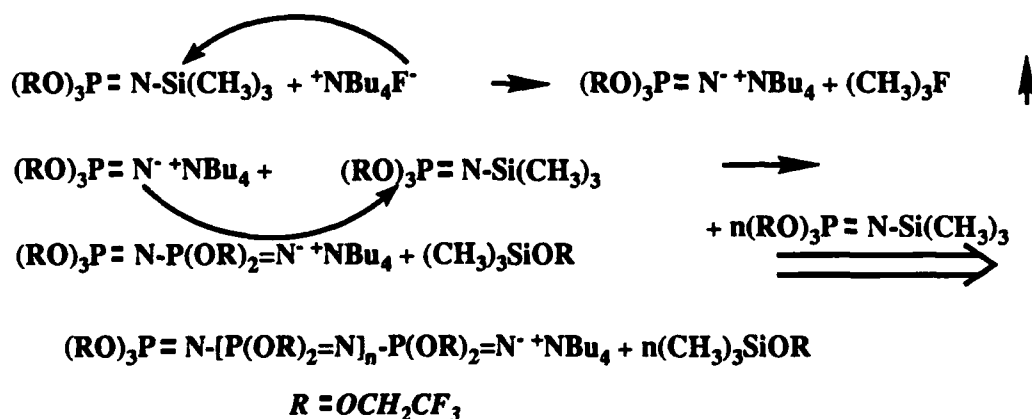


Polyphosphazenes obtained by thermal polymerization of phosphoranimines give linear products with molecular weights in the range of 10,000 to 100,000. No control of molecular weights and no control of end-groups is possible in the thermal process.

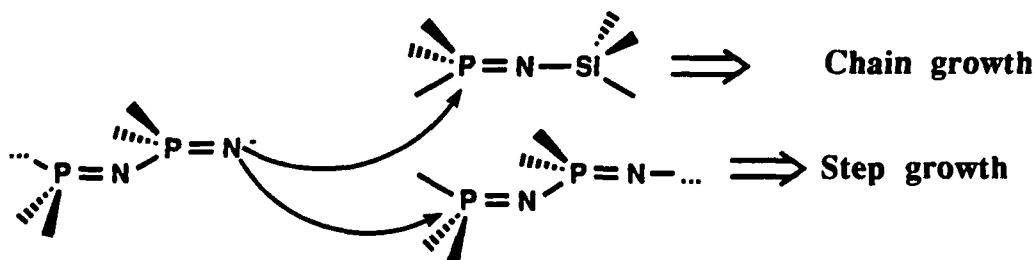
### Catalyzed Polymerization of Phosphoranimines

Thermal polymerization of phosphoranimines has a character of the chain reaction with high polymer formed at low conversion and with noticeable induction periods. We decided to explore possibility of the catalysis in this process. The induction periods indicate that in the initial stage some type of active species is slowly formed which later becomes responsible for the chain growth nature of the process. It is known that silyl group in phosphoranimines has high mobility and that cations of a type  $\text{R}_2\text{P}-\text{N}^+-\text{PR}_2$  are quite stable due to strong delocalization of the

positive charge. Thus, we first assumed that polymerization may have an anionic character and that we should provide initiators which will carry bulky cations and anions with a high affinity towards trimethylsilyl group. The obvious choice was tetrabutylammonium fluoride which tremendously accelerated reaction and provided a high polymer within one hour at 100 °C (compare with a few days at 200 °C for a noncatalyzed process). Polymers with molecular weights ranging from  $M_n=20,000$  to 100,000 were prepared using tetrabutylammonium fluoride and other anionic initiators which include various salts with crowned and cryptated cations. The simplified plausible reaction mechanism is presented in the scheme below<sup>19</sup>:

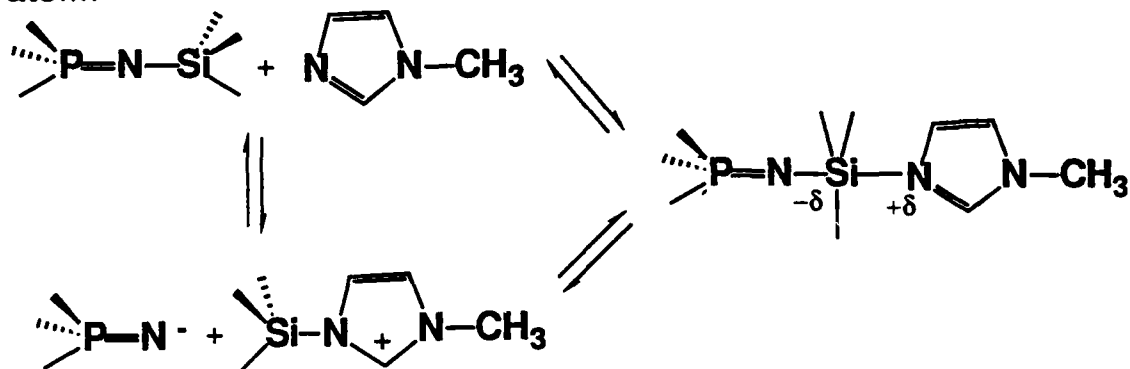


Trimethylsilyl fluoride was detected indeed at the early stages of the polymerization as a volatile product. However, it is possible that the actual propagation step may involve not purely ionic species but active centers with pentacoordinated silicon atom. More detailed kinetic analysis of polymerization as well as change of the molecular weight with conversion indicate that some other reactions also play an important role. Reaction between end groups, not important at the beginning of the reaction (large excess of monomer), leads to increase of molecular weight by interchain condensation:





Another class of effective initiators is based on salt-free systems. N-Methylimidazole, known from its high affinity towards silyl group has been successfully used as the initiator. The role of a cation is then played by the silylated imidazol. This species might be in a dynamic equilibrium with the non-silylated species and intermediate species with a pentacoordinated silicon atom:



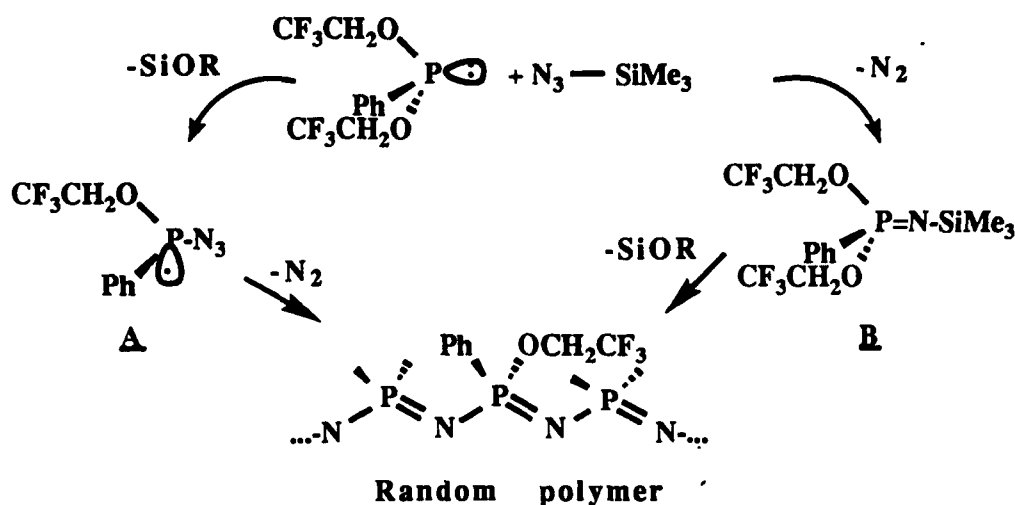
Therefore, imidazole will act more as a catalyst than as an initiator, since it will regenerate in each propagation act. Qualitatively, polymerizations initiated by salts and by imidazole behave in a similar way. Yields are quantitative and NMR indicates a linear polymer structure (>95%). Molecular weight distribution are in the range of  $M_w/M_n \approx 1.2$  to 1.5.

Termination of polymerization of the phosphoranimines with electrophilic reagents such as benzyl bromide leads to the quantitative incorporation of benzyl moiety as the end group into polymer chains. This enables formation of end-functionalized polymers and oligomers based on polyphosphazenes, polymers with unique properties.

Thus, the catalyzed polymerization of phosphoranimines is a potential route to the formation of well defined polyphosphazenes with controlled molecular weight and controlled structure of end groups.

### Polyphosphazenes by Direct Reaction of Silyl Azides with Phosponites and Phosphinites

Reactions of phosphonites and phosphinites with silyl azide have to be carried out with extreme care. In addition to the phosphoranimine, the formation of phosphine azides is observed. These compounds may explosively decompose to polyphosphazenes and nitrogen in a chain process:



The relative proportion of path **A** (phosphine azide) and **B** (phosphoranimine) depends on substituents at phosphorous. Thus, phosphites do not form phosphine azides, phosphonites yield a mixture of products, and phosphinites give nearly exclusively phosphine azides and no phosphoranimines.

The most interesting case is bis(trifluoroethyl)phenylphosphonite which starts to react with silyl azide at 70 °C. The polymerization occurs spontaneously and without catalyst poly(phenyltrifluoroethoxyphosphazene) in up to 80% yield is formed. The remaining 20 % of the phosphoranimine could not be polymerized thermally up to 200 °C. Therefore, polymer can not be formed from phosphoranimine but rather in a parallel pathway **A**. Indeed, the reaction run at 120 °C provides phosphoranimine in 41% preparative yield, and much lower amount of polymer. Apparently pathway **B** has a higher activation energy and is preferred at higher temperatures. This polyphosphazene is an amorphous polymer due to perfectly random microstructure deduced from NMR studies. This polymer has a glass transition temperature at -31 °C, and is thermally stable up to 300 °C.

Reaction of trifluoroethyl diphenylphosphinite occurs explosively in bulk but can be mediated in solution. Poly(diphenylphosphazene) precipitates as a white powder from ethereal solutions. Polymerization is quite sensitive to solvent effects and in alcohols and chlorinated solvents provides mostly oligomers. Similar reaction with diphenylchlorophosphine leads preferentially to cyclics.<sup>20</sup>

The examples presented of the polymerization of phosphoranimines and phosphine azides which were formed *in situ* demonstrate the possibility for the preparation of polyphosphazenes in previously inaccessible range of molecular weights, polymers with increased control of macromolecular

structure (modalities, polydispersities) and new polymers with e.g. diphenyl and phenyl/trifluoroethoxy substituents. It is believed that more thorough studies on new synthetic routes towards polyphosphazenes will enable additional control of microstructure, macromolecular structure and supramolecular structure in these important materials.

### POLYSILANES

Polysilanes are macromolecules with a linear Si-Si catenation in the main chain and with two organic substituents at each silicon atom. They have interesting physical and chemical properties and are of a potential commercial importance<sup>21,22,23</sup>. Poor compatibility of inorganic and organic segments provides morphologies with clear mesophases<sup>24</sup>. Photosensitivity of polysilanes leads to applications in microlithography<sup>22,25</sup>. Strong delocalization of electrons in the backbone provides materials with extremely interesting electronic properties: semiconductors, photoconductors, and nonlinear optical materials<sup>21,22,26,27,28</sup>. However, the synthetic aspect of polysilanes is not yet developed to the level corresponding to their physicochemical characterization. First, and still the most common preparative technique is based on the reductive coupling of disubstituted dichlorosilanes with alkali metals<sup>29,30</sup>. The polymodality of the obtained polymers limits some characterization techniques and also disables some applications<sup>21,22</sup>. The dehydrogenative coupling in the presence of transition metals usually provides low molecular weight materials<sup>31,32</sup>. There are two other routes to polysilanes based on the anionic polymerization of "masked disilenes"<sup>33</sup> and on the ring-opening polymerization<sup>34</sup>. These techniques may provide additional control of the microstructure of the nonsymmetrically substituted systems. In this paper some of our recent activities in the synthesis and characterization of polysilanes will be discussed. These include mechanistic studies of the sonochemical reductive coupling process, ring opening polymerization, and reactions on polysilanes, i.e. modification and grafting, as well as characterization of some copolysilanes.

### Sonochemical Reductive Coupling Process

Polymerization of disubstituted dichlorosilanes with alkali metals via reductive coupling has a strong character of a chain (not a step) process. Molecular weights are very high at low

conversions and independent of the  $[Mt]_0/[Si-Cl]_0$  ratio. Several intermediates such as silylene, radicals, and anions have been proposed as potential chain carriers. Yield of high molecular weight polymer and polydispersities depend very strongly on reaction conditions (stirring rate, solvents, temperature, reducing agent, substituents at silicon atom). The correct choice of initiator and reaction conditions has tremendous influence on the polymerization process.

Under sonochemical conditions (ambient temperature) polymerization has mostly ionic character, although the intermediate radicals could be trapped as a short living species on the pathway from polymers terminated with  $\dots-SiR_2-Cl$  to  $\dots-SiR_2^-$ ,  $Mt^+$  34,35,36. The former participates in two one-electron transfer processes, whereas the latter reacts with a monomer in the nucleophilic substitution process. The exact nature of the Si-Mt bond is still obscure and, under some conditions, it may have a covalent character.

In toluene, using sodium as a reducing agent, monomers with aryl groups react much faster than dialkylsubstituted dichlorosilanes<sup>37</sup>. The latter require elevated temperatures (above 80 °C), although they react readily with Na/K and K.

On contrary, methylphenyldichlorosilane does not react with potassium within 2 hours under similar conditions. This apparent discrepancy has been solved by the analysis of the product of the reaction of phenylmethyldichlorosilane with K at longer reaction times. The resulting polymer ( $M_n \approx 2,000$ ) is not a polysilane. It does not absorb above 300 nm and it contains a large amount of toluene moieties, in contrast to any other polysilanes. GC/MS analysis of the first products formed in this reaction indicates the presence of  $Cl-SiMePh-PhMe$  species, formed via reaction of a monomeric radical with toluene. This result confirms the chain nature of the polymerization in which an electron transfer to a polymer chain occurs much faster than to the monomer. Of course, an electron transfer to methylphenyldichlorosilane from potassium is much faster than from sodium, but initiation is still a few orders of magnitude slower than propagation. Moreover, an electron transfer from potassium may occur from a much longer distance than from sodium (in a way analogous to Grignard reagent formation)<sup>28</sup>. Therefore, the monomeric radicals may be separated by two or three solvent molecules from the metal surface and, instead of the coupling process or the second electron transfer, they react

with toluene or diffuse to the bulk solvent. Reaction of silyl radicals with toluene is very fast ( $k=1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ )<sup>39</sup>.

Reductive coupling at ambient temperatures in the presence of ultrasound leads to monomodal polymers with relatively narrow molecular weight distributions ( $M_w/M_n$  from 1.2 to 1.5) and relatively high molecular weights ( $M_n$  from 50,000 to 100,000)<sup>37</sup>. There are two phenomena responsible for the more selective polymerization. First, lower polymerization temperature and continuous removal of the sodium chloride from the sodium surface suppresses formation of the low molecular weight polymer ( $M_n$  from 2,000 to 10,000). This polymer might be formed via some side reactions (transfer or termination). Second, ultrasound mechanically degrades polysilanes with molecular weights above 50,000. This limit might be set by the chain entanglement and Si-Si bond energetics. Polysilanes prepared in separate experiments could also be selectively degraded. It seems that degradation in toluene in the presence of alkali metals is slightly accelerated, but no low molecular weight cyclooligosilanes are formed. On the other hand, in THF and diglyme (or in toluene in the presence of cryptands and potassium) polymer is completely degraded to cyclohexasilanes and cyclopentasilanes. The anionic intermediates have been observed spectroscopically in this degradation.

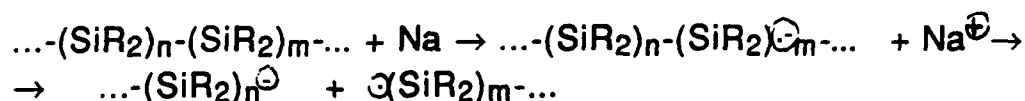
Copolymerization of various dialkylsubstituted dichlorosilanes by a reductive coupling process usually leads to statistical copolymers<sup>40</sup>. The copolymer composition usually corresponds to the monomer feed and the distribution of various triads, pentads, and heptads roughly corresponds to Bernoullian statistics.

Polysilanes are usually prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals in non polar solvents such as toluene or hexane. No substantial degradation of the polymer is observed in the presence of an excess of alkali metal in these solvents. Polymers with higher molecular weights are prepared in solvents of lower solvating ability. Polysilanes can be degraded by an excess of alkali metal in THF or in diglyme. Cyclic oligomers are the only degradation products. The rate of degradation depends on the substituents at the silicon atom, solvent, alkali metal, and temperature. Degradation is much faster in more polar THF than in toluene. Addition of cryptand [2.2.2] or THF to toluene increases the degradation rate. The rate of degradation strongly increases with the reactivity of the metal. Electron transfer from potassium is much easier than

from sodium or from lithium. The effect of the counterion seems to be less important, since degradation initiated by sodium or lithium naphthalides proceeds nearly as fast as with potassium. On the other hand, the initial electron transfer process is strongly metal dependent. The application of the ultrasound helps to clean the metal surface by cavitation erosion but does not change the rate of degradation. Degradation is much faster for poly(methylphenylsilylene) than for poly(di-n-hexylsilylene). This is in agreement with the general trend in the stability of silyl anions discussed in the previous section. Aryl groups on the silicon atom stabilize anionic intermediates. A counterion effect on the degradation is observed. Degradation with  $K^+$  is faster than with  $Na^+$  or  $Li^+$ . Moreover, lithium can not start the degradation process. Even in THF solution the first electron transfer is not possible. This may be due to surface phenomena since lithium naphthalide degrades polysilylenes efficiently.

During chemical degradation cycles are formed but the molecular weight of polysilylenes does not change. This indicates a chain process with slow initiation and fast propagation.

The first step in which a polymeric radical anion is formed should be rate limiting. It is facilitated in more polar solvents due to the energy gain by the solvation of alkali metal cations. The intermediate radical anion cleaves to a radical and an anion. The fate of the radicals is not known. They may react with a solvent, take a second electron to form a silyl anion, or recombine, although radical concentration is usually very low. The silyl anions may now start cleaving Si-Si bonds:



The rate of the intramolecular reaction must be much faster than the rate of the intermolecular process due to entropic effects. The anchimeric assistance (or neighboring group participation) is the highest for the least strained five- and six-membered rings. Therefore, the degradation process leads to cyclopentasilanes and cyclohexasilanes. The back-biting process for larger or smaller rings is retarded for enthalpic reasons. The back-biting process has to be distinguished from the end-biting process which may occur during the synthesis of polysilylenes. Additional evidence for different mechanisms of end-biting and

back-biting processes are provided by the structure of cyclic oligomers which are formed during the synthesis of poly(di-n-hexylsilylene). Above 80% of octa-n-hexylcyclotetrasilane ( $\delta = -20.3$  ppm in  $^{29}\text{Si}$  NMR) is formed under the reductive coupling process in a mixture of toluene and isooctane. On the other hand, the degradation leads to the formation of deca-n-hexylcyclopentasilanes ( $\delta = -34.6$  ppm).

The present results clearly indicate that back-biting (or degradation) is not important in toluene in the absence of any additives. It is also not very important for poly(di-n-hexylsilylene) in THF. However, polymerization of methylphenyldichlorosilane with any alkali metal in THF will result in cyclics rather than in a linear polymer.

Thus, the correct choice of the conditions of reductive coupling and the structure of the reducing agent is extremely important in determining yields and molecular weight distribution of final products.

#### Ring-Opening Polymerization

Reductive coupling of disubstituted dichlorosilanes with alkali metals is usually accompanied by the formation of cyclooligosilanes. Under some conditions, a linear polysilane can be completely degraded to cyclics. Thus, a polysilane can be considered as a kinetic product, whereas cyclic oligomers are true thermodynamic products. The majority of known cyclooligosilanes are thermodynamically stable and cannot be converted to linear polymers. Some potentially strained rings such as octaphenylcyclotetrasilanes can be prepared in high yield since the repulsive interactions between phenyl groups present at each silicon atom have a greater influence than the angular strain in the four membered ring. Additionally, low solubility and high melting point (mp.  $\approx 323^\circ\text{C}$ ) precludes polymerization of octaphenylcyclotetrasilanes at higher concentrations. We have discovered rapid and clean Si-Ar bond cleavage with trifluoromethanesulfonic acid<sup>41</sup>. Reaction of octaphenylcyclotetrasilanes with four equivalents of the acid leads to 1,2,3,4-tetra(trifluoromethanesulfonyloxy)-1,2,3,4-tetraphenylcyclo-tetrasilane. Subsequent reaction with either methylmagnesium iodide or methyl lithium yields four stereo isomers of 1,2,3,4-tetraphenyl-1,2,3,4-tetramethylcyclotetrasilane.

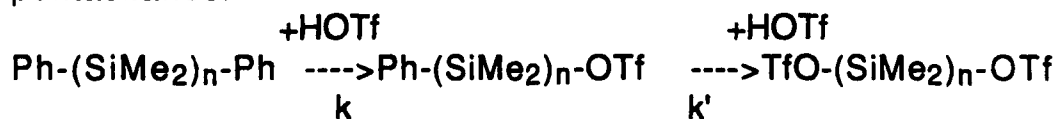
A Si-Si bond is quite labile in the presence of strong electrophiles and nucleophiles. Reaction with silyl anions leads

to ring-opening and to the regeneration of silyl anions<sup>42</sup>. This is the propagation step. Silyl anions may also attack the Si-Si bonds in the polysilane chain and form macrocycles and strainless cyclooligosilanes. Rates of polymerization and degradation depend on solvent, temperature, and alkali metals. With 1 mol% of silyl potassium or butyl lithium initiator, only cyclooligosilanes have been found after less than 2 minutes at room temperature in pure THF. In benzene, with less than 3% THF, polymerization is completed after more than 1 hour. In mixtures of 60 % THF with benzene polymerization is completed within less than 2 minutes, but degradation starts after 1 hour. Polymers with molecular weights from 10,000 to 100,000 have been prepared via the anionic ring-opening polymerization of cyclotetrasilanes. This technique provides a pathway to various functional polymers and block copolymers.

In this system the proper choice of solvent, temperature, and counterion determines yields and distribution of products. Non polar solvents provides higher yields and higher molecular weights of polymers. More polar solvent lead to much faster polymerization but also to much faster degradation to strainless cyclic oligomers.

#### Modification of Poly(phenylmethylsilylene)

The severe conditions of the reductive coupling process and the anionic process allow only alkyl and aryl substituents at silicon. There are only a few polysilanes known with substituents other than alkyl and aryl. However, the Si-Ph bond can be easily cleaved by strong protonic acids such as triflic acid. The rate of the dearylation is strongly influenced by the presence of an electron withdrawing group at the neighboring Si atoms. Model studies on dearylation of  $\alpha,\omega$ -diphenylpermethyloligosilanes with triflic acid indicate that the displacement of the first phenyl group is always faster than that of the second, even for pentasilanes:



$k/k' = 23, 13, 10, 7$  for  $n = 2, 3, 4, 5$

Apparently, the reactivity of the oligosilanes increases with the chain length in contrast to the electron density on the *ipso*-C atom which is attacked in the rate determining step. This



indicates that the transition states rather than the ground states control reactivities of polysilanes.

The dearylation process applied to polysilanes containing phenyl substituents provides polymers with strong electrophilic silyl triflate moieties. Silyl triflates belong to the strongest known silylating reagents. They react with ketones  $10^8$  times faster than silyl chlorides do. They can react with any nucleophiles such as alcohols, amines, carbanions, organometallics, etc. This opens a new synthetic avenue towards various functional polysilanes<sup>35,43</sup>. The reactivity of silyl triflates is so high that they can initiate cationic polymerization of some alkenes and heterocyclics to form graft copolymers.

Silylated triflate backbone is very reactive and triflate groups can be easily displaced by a variety of nucleophiles such as alcohols, amines, organometallic reagents, etc. This chemistry resembles the modification of chlorinated polyphosphazenes. A variety of functional groups lead to new materials which are lipophobic, hydrophilic, and some of them show additional phase ordering. For example, the attachment of a p-methoxybiphenyl mesogen via long flexible spacer with six methylene units to partially triflated poly(methylphenylsilylene) leads to modified polysilanes with liquid crystalline behavior. Shorter spacers and weaker mesogens form only isotropic materials. Probably inherent incompatibility of the main chain and side groups as well as the rod-like behavior of polysilanes prevent ordering of side chain mesogen groups in most systems.

#### Copolysilanes with Chiral Substituents

It is well established that polysilanes with two identical alkyl groups formed at ambient temperatures regular crystalline structures. Various analytical techniques identified the extended zig-zag conformation for di(n-hexyl) derivative, but 7/3 helical structure for di(n-pentyl) and di(n-butyl) derivatives. The ordered crystalline phase is still accompanied by a typical chain folding since single crystals with a typical screw-dislocation are formed from poly(di-n-pentylsilylene) as shown in Fig. 1. A micrograph of a larger amount of these crystals indicates (as expected) that an equal amount of crystals with left-handed and right-handed dislocation are present.

It was of interest to control supramolecular structure of these crystals and to prepare all crystals with one-sense dislocation. This was accomplished by incorporation of 5 to 20% of chiral 2-methylbutyl (isopentyl) groups into poly(di-n-

pentylsilylene). Fig. 2 shows a micrograph of a collection of single crystals with a one-sense dislocation formed from the copolymer with a 5% content of chiral units.

These copolymers show relatively weak optical activities in solution and the optical rotation is approximately 50 times higher than predicted from the content of chiral substituents. The molar optical rotations increase with a decrease of temperature and become very large after addition of a non solvent (isopropanol). Polysilanes adopt a random coil structure in solution and there is only a small proportion of a helically oriented chromophores, especially at low proportion of chiral unit (every 10 or every 20 silicon atoms). However, at lower temperatures and at limited solubilities, a helical structure is formed which is accompanied by a dramatic increase in optical activity (100 times or 5,000 times based on optical activity of isolated chiral unit). This increase can be also partially ascribed to the intermolecular coupling of chromophores.

In agreement with this explanation, solid films of the copolymers with chiral groups exhibit strong optical activities and strong ellipticities as determined by circular dichroism. (Fig. 3).

Thus, as demonstrated in the above examples using sonochemical reductive coupling, ring-opening polymerization, and modifications it is possible to prepare new interesting polysilanes with regular structures. Correct choice of initiators and catalysts is in these systems very important.

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### Captions for Figures:

Fig. 1. Electron micrograph of a single crystal of poly(di-n-pentylsilylene). Magnification 20,000. Crystals were shaded with Pt/C to enhance contrast.

Fig. 2. Electron micrograph of single crystals of poly(di-n-pentylsilylene-co-di-isopentyl\*silylene). Helical growth of lamellae in one direction may be assigned to the presence of the chiral units (10%).

Fig. 3. Circular dichroism of thin films ( $\approx 100$  nm) of poly(di-n-pentylsilylene-co-di-isopentyl\*silylene) (95:5)

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**CD SPECTRUM OF THIN FILM ( $\approx 100$  nm)  
OF POLY[(DPS)<sub>0.95</sub>-co-(DiP\*S)<sub>0.05</sub>]**

